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Effect of the different chain transfer agents on molecular weight and optical properties of poly(methyl methacrylate)

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A B S T R A C T

Investigation of molecular weight and optical properties of poly(methyl metacrylate) (PMMA) polymerized in house with different chain transfer agents was studied. Isopropyl alcohol (IPA), n-butyl mercaptan (nBMC) and pentamethyl disilane (PMDS) were used as chain transfer agents. The molecular weight (M_w) of PMMA samples were measured by Ostwald viscometer. M_w of bulk polymer samples were decreased with increase the concentration of chain transfer agents (CTA). Since reactivity of used CTAs is not same, molecular weights of samples which were produced with different type of CTA but same concentration of CTA was varied. Higher concentration of n-BMC showed higher scattering. Transmission of samples could not be correlated with different concentration of CTA. Refractive index of samples was not affected by concentration of CTA nevertheless higher molecular weight of CTA showed higher refractive index.

1. Introduction

Optical polymers are useful material instead of silica with many properties for short haul communications such as lower cost, larger core-diameter and, easy handling, low weight, multiplexing capabilities [1,2]. PMMA is a preferred polymer for manufacturing polymer optical fibers and for applications [3–8] with better elastic limit (10%) according to silica (1–3%) and can stand up to 30% strains [9]. Due to impurities and intrinsic absorption [10] caused by C–H bonds [11], PMMA is not favorable material according to silica in long distance applications.

In polymer optical fiber technology, polymers should have proper molecular weight (Mw) for proper drawing process. Radical chain transfer reactions are suitable for controlling M_w of polymers [12]. For this purpose, mechanism and kinetic of chain transfer agents were investigated by many researchers [13–19]. Additionally, chain transfer agents have also effect on structure of polymer which causes to changes heating resistance [20].

Thiols derivatives are commonly used as a CTA due to weakness of S–H bond [21,22]. For vinyl monomers, e.g. methyl methacrylate and styrene, thiols are effective CTA [23].

Controlled pseudo-living radical polymerization studies were done by Korolev et al. and Zaremskii et al. to obtain monodisperse polymers but because of reversible inhibition the polymerization rate is low [24,25]. For producing polymer with narrow molecular weight distribution, Semchikov et al. used polyfunctional silicon hydrides to solve problem [26]. Instead of mercaptans which are well-known CTA, Bulgakova et al. used organohydrodisilanes which are more effective [27,28]. In another study of Bulgakova et al., they employed silicon hydrides as CTA and compared the reactivity of silicon hydrides for M_w of styrene and methyl methacrylate [29]. As a conclusion of this study, the reactivity of organosilicon hydrides is related with chemical structure of CTA and the activity of monomer.

Okay et al. employed IPA as chain transfer agent to control the average number of segments in a network chain. As concentration of IPA is increased, the chain length of the primary chains is decreased and they indicated that the average number of segments in a network chain is highly related with IPA concentration [30].

Investigation of the effects on optical properties of PMMA bulk polymer samples to use in optical fibers technology was presented. Different concentration of three CTAs were employed to fabricate proper bulk polymer samples. It was aimed to analyze optical properties of PMMA polymer samples depending on polymer structure which is affected by different structured CTAs. In literature, effect of chain transfer agents on optical properties of

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polymers was not compared. For this purpose, molecular weight, transmission and refractive index of bulk samples were measured and also scattering which was done by green laser was observed.

2. Materials and methods

Methyl methacrylate (MMA, 99%, Aldrich) was used as monomer after purification via vacuum distillation method. Benzoyl peroxide (BPO, 75%, Aldrich) was purified and employed as initiator. Isopropyl alcohol (IPA, 99.9%, Fluka) and n-butyl mercaptan (nBMC, 99% Signa-Aldrich), Pentamethyldisilane (PMDS, 97%, Aldrich) were selected as CTA and only PMDS was purified with silica column (Silica gel 60, 70–230 mesh, Merck). The purity of PMDS was measured by gas chromatography (GC, Shimadzu GC-2010) and it was found 98.3%. In all studies for measuring M_w, chloroform (98.5%, POCH Basic) was employed as solvent without any purification.

3. Experimental

3.1. Polymerization

The monomer (MMA), initiator (BPO, 0.4%) and CTA (IPA, nBMC or PMDS) were mixed in glass test tube and thermal bulk polymerization was carried out (Fig. 1). In order to demonstrate effect of purification both purified and non-purified PMDS were used.

3.2. Characterization

3.2.1. Molecular weights

Molecular weights of PMMA samples with different chain transfer agents were measured by Ostwald viscometer in chloroform at 30 °C. The M_w of PMMA samples were calculated by following formula, [31].

$$[\eta] = 4.9 \times 10^{-5} \times M_w^{0.8} \quad (1)$$

where η is viscosity of solution of PMMA sample in chloroform and M_w is molecular weight of PMMA sample.

3.2.2. Optical properties

Bulk PMMA samples were cut as cylindrical with 1 cm radius and 1.6 cm length and optically polished from both front side to use in transmission and refractive index measurements and observing of scattering. Optical transmission measurements were done between 340 and 1100 nm wavelengths. Scattering studies were made by green laser (534 nm wavelength). In refractive index measurement Abbe refractometer (measurement accuracy - ±0.0001) was used.

4. Results and discussion

4.1. Effect of chain transfer agent on molecular weight

One of the purpose in this study is producing polymer for optical fiber technology. Commercially available PMMA which is used for fabricating optical fiber is around 100,000–150,000 g/mol. Therefore, M_w of bulk polymer samples should be in this range and concentration of CTA should be low as far as possible for avoiding impurities.

CTAs which arrange polymer chains during polymerization control the M_w. There is a relative inversely between concentration of chain transfer agent and M_w of polymer. (Fig. 2).

Due to different reactivity of varied CTAs, it is caused to have different M_w of polymer samples which were produced with same concentration of CTA [17,32].

According to molecular weight results, optimum CTA is n-BMC to produce polymer which is in desired M_w range with lower concentration of CTA (Fig. 2(b)). It can be considered that optical loss due to compounds besides PMMA in polymer structure was minimized. PMDS is also suitable CTA in this range. In Fig. 2(a), minimum M_w of polymer sample which was produce with IPA was reached to above of commercial PMMA and concentration of CTA was not increased due to avoid from optical loss.

In comparison of purified and non-purified PMDS, in Fig. 2(a) and (b), it can be seen clearly that purified PMDS has better slope than non-purified PMDS. Impurities could cause inhomogeneous polymerization. Homogeneous polymerization is highly important to have proper polymer for optical fibre technology.

4.2. Optical results

In scattering studies, green laser (534 nm) was used to observe the effect of chain transfer agent on scattering behavior. Intensity of

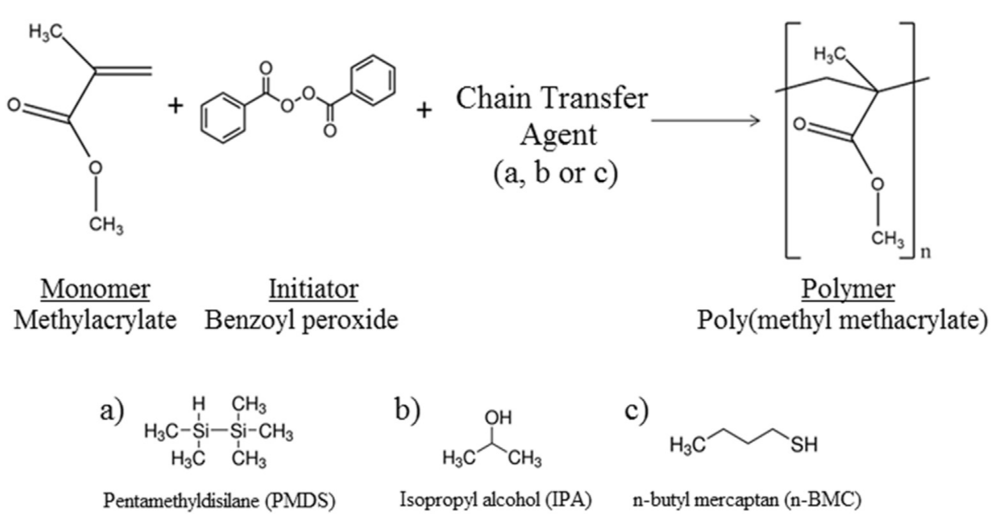

Fig. 1. Reaction of polymerization of MMA with CTAs.